Sulphide-induced deactivation of Pd/Al$_2$O$_3$ as hydrodechlorination catalyst and its oxidative regeneration with permanganate

Dalia Angeles-Wedler, Katrin Mackenzie, Frank-Dieter Kopinke *

UFZ – Helmholtz-Centre for Environmental Research, Department of Environmental Technology, Permoserstrasse 15, D-04318 Leipzig, Germany

ARTICLE INFO

ABSTRACT

Pd-based catalysts have become important in environmental catalysis for their ability to hydrode-chlorinate a wide range of chlorinated organic contaminants in water under ambient conditions. The success of their application in the remediation practice, e.g. for groundwater treatment, is often hindered by the sensitivity of Pd to poisoning by sulphur compounds. In this study, the stability and sulphide-induced deactivation behaviour of a highly active Pd/Al$_2$O$_3$ catalyst was investigated. The specific activity of Pd for the hydrodechlorination of chlorobenzene corresponds to rate coefficients up to k_{Pd} = 350 L g^{-1} min^{-1}. The totally deactivated catalyst, resultant of sulphide poisoning, was regenerated with potassium permanganate. The pH value, as a key parameter which may influence the degree of deactivation as well as the efficiency of catalyst regeneration, was evaluated. Results show that in clean water the Pd/Al$_2$O$_3$ catalyst showed no inherent deactivation regardless of the ageing time and the pH value of the catalyst suspension. The degree of catalyst poisoning effected by 1.8–5.4 μM sulphide, corresponding to molar ratios of S:Pd$_{surface}$ = 1.5–8.5, was observed to be higher under neutral and alkaline than under acidic conditions. The exposure of the catalyst to higher sulphide concentration of 14.2 μM resulted in complete catalyst deactivation regardless of the pH conditions. However, the efficacy of permanganate as oxidative regenerant for the fouled catalyst showed strong pH-dependence. A regeneration time of 10–30 min at low pH was sufficient to recover completely the high catalytic activity of Pd/Al$_2$O$_3$ for the hydrodechlorination reaction.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Palladium-based reagents have become important in environmental catalysis whereby halogenated contaminants are transformed to less or non-harmful compounds. Together with an electron donor (e.g. H$_2$ or HCOOH), Pd catalytically reduces chlorinated organic compounds according to the chemical equation R-X + H$_2$ $\xrightarrow{Pd}$ R-H + HX. Pd catalysts, unlike Fe-based dechlorination, can reduce a wide range of chlorinated aliphatic as well as aromatic contaminants with high turnover frequencies in the order of 1 s^{-1} at ambient conditions. This high inherent catalytic activity delivers half-lives of only a few seconds to minutes for the batch hydrodechlorination of C$_1$- to C$_3$-halogenated aliphatics and halogenated aromatic compounds such as chlorobenzene [1–4]. The dechlorination reaction proceeds to completion, preventing the accumulation of partly dechlorinated by-products which are in some cases more toxic than the parent compounds. To date, Pd-based bimetallic catalysts are finding wider application in terms of promoting nitrate reduction and the

chemical reduction of emerging water pollutants such as N-nitrosodimethylamine and perchlorate [5–7].

Regarding field application, Pd-catalyzed hydrodechlorination is drawing researchers' attention as a promising alternative for the *in situ* treatment of chlorinated contaminants in water. Pd-based reactors have been tested in the field, including the construction of a reactive well system, column reactors and Pd-based membrane reactors for the treatment of contaminants such as TCE, PCE and chlorobenzene [8–12]. During these field-test studies, the dechlorination rate of the contaminants was significantly reduced over the time of operation due to poisoning of Pd catalysts by reduced sulphur compounds (e.g. sulphides). Sulphides are known to have a strong affinity for Pd metal and may block the active sites of the catalyst via formation of strong Pd–S bonds and adlayers of sulphide around the Pd clusters [13–15]. Since sulphide is a natural water constituent under reducing conditions produced via microbial sulphate reduction, sulphide-induced catalyst deactivation is a crucial issue which hinders the full exploitation of the catalyst potential as a treatment technology for groundwater remediation. One alternative approach to prevent sulphide poisoning is the removal of sulphide prior to any contact with the noble metal. This can be achieved by oxidative water pre-treatment with permanganate in order to oxidize sulphides to

---

* Corresponding author.
  E-mail address: frank-dieter.kopinke@ufz.de (F.-D. Kopinke).

sulphate, which does not negatively affect the dechlorination reaction [16].

Nevertheless, in any case of catalyst deactivation it is necessary to have a simple and efficient regeneration procedure to recover catalyst performance. The common regeneration procedure for sulphide-fouled Pd catalysts used in gas-phase reactions is a high-temperature treatment with hydrogen [17–20]. This process is, however, unsuitable for catalysts used in the water phase. So far, the only method which has showed relative success in the liquid-phase regeneration of sulphide-fouled Pd catalysts is an oxidative treatment with hypochlorite [21–23]. This procedure requires long regeneration times or multiple regeneration cycles. Other oxidants such as heated air and H_2O_2 have only delivered limited success [21,23], while the use of Fenton's reagent and Peroxone $(H_2O_2 + O_3)$ showed no success (unpublished own results). In the present study, the sulphide-induced deactivation and the permanganate-induced regeneration of Pd/Al_2O_3 were investi-gated, with a special focus on the pH-dependence of both processes. Obviously, the sulphur speciation also depends on the pH value (for H_2S: $pK_{A1} = 7.05$, $pK_{A2} \approx 13$, with differing values in the literature). The hydrodechlorination (HDC) performance of fresh, poisoned, and regenerated catalysts was tested, whereby monochlorobenzene (MCB) was used as the probe compound.

2. Experimental

2.1. Chemicals

MCB (99.8%) and $Na_2S \cdot 9H_2O$ (reagent grade) were obtained from Sigma–Aldrich. $KMnO_4$ (extra pure crystalline) was supplied by Merck. A commercially available egg-shell Pd on γ-Al_2O_3 catalyst (G-133 D purchased from Commercia, Germany) with 0.51 wt% Pd (from EDXRF analysis), a BET surface area of $140 \, m^2 \, g^{-1}$ (N_2 adsorption) and a Pd dispersity of 0.17 (CO adsorption) was used. The original 3 mm pellets were crushed and sieved. The 25–63 μm fractions were pre-conditioned in the aqueous phase by purging with hydrogen gas under atmospheric pressure (i.e., $p_{H_2} = 100 \, kPa$).

2.2. Catalyst activity and stability

The HDC of MCB over Pd/Al_2O_3 was conducted as batch experiments using 250-mL amber screw-cap bottles equipped with Mininert® valves. The general procedure for preparing a batch reaction included the addition of 30 mg of pre-reduced Pd/ Al_2O_3 into the batch bottle containing 200 mL deionized water (DW), HCl-amended DW (for pH 3) or NaOH-amended DW (for pH 13). The resulting catalyst suspension was then purged with He for 1 h, after which the headspace was exchanged with hydrogen gas without mixing the water phase. A defined volume of MCB stock solution was spiked into the batch bottle, giving a concentration of 20 mg L^{-1}. The bottle was shaken (180 rpm in a horizontal shaker) to start the HDC reaction. Repeated batch runs were conducted on the same catalyst suspension after 0–16 days standing (catalyst ageing). Before each run, the benzene product of the preceding reaction was purged-out with He. Hydrogen gas and MCB were then freshly added into the reaction bottle. The kinetics of the HDC reaction was followed via educt disappearance and product formation. Both were monitored via headspace analysis (25 μL gas tight syringe) using a GC–MS QP2010 (Shimadzu). In all cases, the MCB disappearance and the benzene formation followed identical kinetics. It is worth mentioning that for low conversion degrees (especially utilized for experiments with low catalyst activities) tracing the benzene yields more accurate data, whereas for high conversion degrees tracing the MCB gives more reliable results.

2.3. Catalyst poisoning and regeneration

The catalyst suspension prepared as described above (30 mg Pd/Al_2O_3 in 200 mL DW with the corresponding pH) was purged with He for 1 h. Afterwards, a defined volume of Na_2S stock solution was spiked into the batch bottle to give the desired sulphide concentration, ranging from 1.77 to 14.2 μM. These concentrations correspond to S:Pd = 0.25 and 2 moles per mole, respectively. Taking into account the Pd dispersity of 0.17 and that S is exclusively bound to the outer Pd surface, the corresponding ratios are S:Pd$_{surface}$ = 1.5 and 12. The batch bottles were shaken overnight in order to effect sulphide-induced catalyst deactivation. The fouled catalysts were tested for their remaining activities by adding hydrogen and MCB. For the totally deactivated catalyst (S:Pd = 2), oxidative regeneration was conducted by spiking an aqueous solution of $KMnO_4$ into the bottle, giving the desired initial concentration of 0.18 mM. The bottle was left to shake on a horizontal shaker at 180 rpm for a defined time period. Afterwards, unconsumed permanganate in the bulk solution was quenched by adding hydrazine until the pink colour had disappeared com-pletely. Hydrogen and MCB were then added in order to test catalyst activities. The changes in pH values during the periods of poisoning, regeneration and HDC reaction were all noted.

3. Results and discussion

3.1. Catalyst baseline activity and stability in clean water

The catalyst performance for the HDC reaction of a contaminant i is expressed in terms of the specific Pd activity $A_{Pd,i}$ according to the following equation [24]:

$$A_{Pd} \, (L \, g^{-1} \, min^{-1}) = \frac{V_{water}}{m_{Pd}\tau_{1/2}} = \frac{\ln(c_{t1}/c_{t2})}{\ln 2 \cdot c_{Pd} \cdot (t_2 - t_1)} \quad (1)$$

where V_{water} is the volume of contaminated water applied, m_{Pd} is the mass of Pd and $\tau_{1/2}$ is the half-life of the contaminant as obtained from its disappearance kinetics. The chosen sampling times t_1 and t_2 correspond to the contaminant concentrations c_{t_1} and c_{t_2}. In the case of simple kinetics, the numerical value for $A_{Pd,i}$ is equivalent to a second-order rate coefficient according to $k_i = \ln 2 \cdot A_{Pd,i}$ with $dc_i/dt = -k_i \cdot c_i \cdot c_{Pd}$.

Typical HDC kinetics of MCB over Pd/Al_2O_3 are shown in Fig. 1. All the reactions, conducted under various pH conditions, follow first-order kinetics with respect to the concentration of MCB up to high conversion degrees (>99%). The catalyst activity is higher under basic conditions ($A_{Pd} = 250 \, L \, g^{-1} \, min^{-1}$ at pH 13) compared
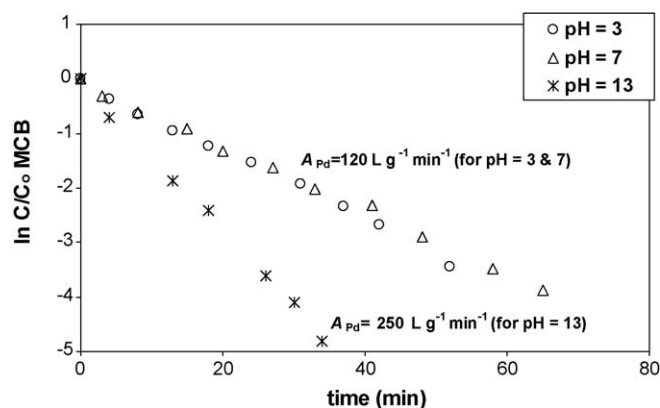
Fig. 1. Kinetics of the hydrodechlorination of chlorobenzene, and catalyst activities (A_{Pd}) under various pH conditions. Deionized water (DW) was used for pH 7, HCl- and NaOH-amended DW for pH 3 and 13, respectively ($c_{cat} = 150 \, mg \, L^{-1}$, $c_{0,MCB} = 20 \, mg \, L^{-1}$).

to acidic conditions (A_{Pd} = 120 L g^{-1} min^{-1} at pH 3). However, the difference is only a factor of 2. This is significant, but not drastic. Due to the lack of an appropriate buffer system which does not disturb the catalytic system, the HDC reaction under neutral start conditions gave rise to slightly decreasing pH values (pH$_{end}$ ≈ 4). A fraction of the released protons was buffered by the catalyst carrier alumina. The catalyst activities calculated from these reaction kinetics are taken as the reference or 'baseline' activities of Pd/Al$_2$O$_3$ in clean deionized water. The beneficial effect of elevated pH values or adding a base (e.g. NaOH) during the HDC reaction is known and has been described in various studies [4,25,26], but this effect is outside the scope of the present study.

A stable activity of the Pd/Al$_2$O$_3$ catalyst for repeated batch HDC runs in a broad pH range (from 3 to 13) is demonstrated in Fig. 2. It should be noted here that the repeated batch runs were conducted on the same catalyst samples and in the same reaction mixtures. Additionally, the catalyst was left to stand in the bulk solution for 0–16 days (catalyst ageing) before each experiment. There are several factors that might deactivate the catalyst due to ageing and prolonged use, e.g. dissolution of Pd under strongly acidic conditions or unfavourable morphological changes in the Pd clusters. Obviously, such inherent deactivation phenomena are not significant in clean water, irrespective of the applied pH value. This is an important technical implication when the Pd/Al$_2$O$_3$ catalyst is to be applied for long-term operation in water treatment processes.

3.2. Sulphide-induced deactivation of Pd/Al$_2$O$_3$

The addition of sulphide to the catalyst suspension resulted in the expected poisoning of the catalyst. Table 1 gives a compilation of the deactivation effects observed. A trace level of sulphide (1.77 μM, S:Pd$_{surface}$ = 1.5 moles per mol) already significantly reduced the catalyst activity in all experiments conducted. The degree of catalyst deactivation depends on the pH value: it is a factor of 10–12 at pH ≥ 7 vs. a factor of 3.6 at pH 3. When the sulphide concentration in the catalyst suspension was increased, the degree of catalyst deactivation also increased. Again, the effects are more pronounced at pH ≥ 7 than under acidic conditions. This points to a stronger poisoning effect of HS$^-$ (and possibly of S^{2-}) than of H$_2$S. The exposure of the catalyst to high sulphide concentrations (i.e. 14.2 μM, giving S:Pd$_{surface}$ = 12) resulted in the total and permanent deactivation of the catalyst regardless of the pH value during the poisoning procedure.

The influence of the pH value on the sulphide-induced deactivation of Pd on γ-alumina has been reported in Ref. [23]. Munakata and Reinhard observed a faster deactivation at lower pH (i.e. 4.8) and a non-zero steady state activity under alkaline conditions (i.e. pH 9.6–10.4). The influence of the pH value on the deactivating effects of sulphide species can be discussed in the
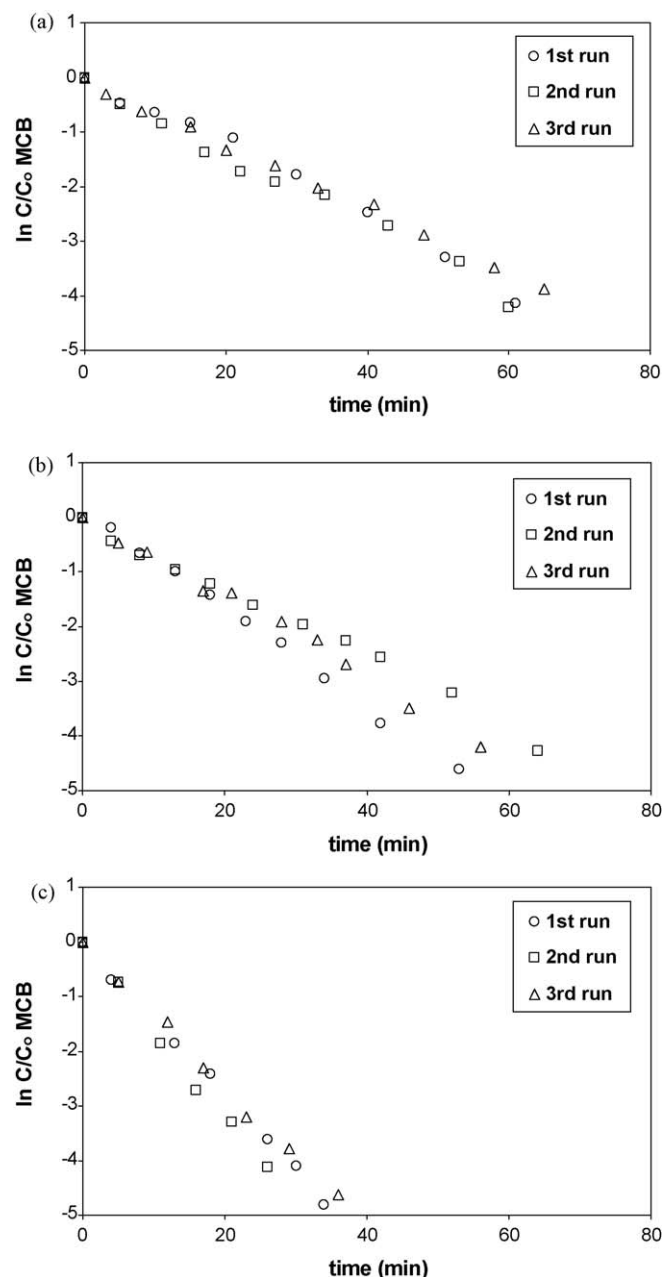
Fig. 2. Stability of the Pd/Al$_2$O$_3$ catalyst performance during repeated runs of hydrodechlorination of chlorobenzene under various pH conditions. The 1st, 2nd, and 3rd runs were conducted on the same catalyst sample after 0, 6, and 16 days of catalyst ageing, respectively, in the aqueous reaction medium. (a) pH 7 (DW), (b) pH 3 (HCl-amended DW), and (c) pH 13 (NaOH-amended DW). Applied concentrations: c_{cat} = 150 mg L^{-1}, $c_{0,MCB}$ = 20 mg L^{-1}.

light of two phenomena: the sulphur speciation and the surface charge of the catalyst. The sulphur speciation is determined by the two pK_A values of H$_2$S (7.05 and ca. 13), whereas the surface charge of alumina is characterized by its pH-dependent zeta-potential and its point of zero charge (pH$_{pzc}$). For the Pd/Al$_2$O$_3$ under study we found pH$_{pzc}$ = 8.2 by means of potentiometric titration [27]. Reported values of pH$_{pzc}$ of γ-alumina range between 7 and 9, depending on thermal activation and impurities [28]. From the point of view of electrostatic interactions, higher pH values are unfavourable for sulphide binding, because the catalyst surface and the sulphur species (HS$^-$ and S^{2-}) are both negatively charged. However, the deactivation experiments showed the opposite tendency. Therefore, we conclude that bisulphide (and possibly

Table 1
Specific catalyst activities (A_{Pd}) for the hydrodechlorination of chlorobenzene in the presence of sulphide under various pH conditions. Deionized water (DW) was used for neutral conditions (pH 7), HCl- and NaOH-amended DW for pH 3 and 13, respectively (c_{cat} = 150 mg L^{-1}, $c_{0,MCB}$ = 20 mg L^{-1}).

Conc. of sulphide (μM)	A_{Pd} (L g^{-1} min^{-1})		
	DW	pH 3	pH 13
0	120 ± 20[a]	120 ± 20	250 ± 40
1.77	10	33	26
3.55	4	20	10
5.35	0.1	3	0.6
14.2	<0.01	<0.01	<0.01

[a] Average deviation of the single values from the mean value originating from three parallel batch experiments.

sulphide) have a stronger affinity to Pd than the non-charged H_2S, which is the exclusive sulphur species at pH 3.

3.3. Regeneration of sulphide-fouled Pd/Al₂O₃ with permanganate

For regeneration of the fully sulphide-deactivated Pd/Al_2O_3 catalysts (S:Pd = 2), permanganate was utilized. An efficient regeneration is only possible when the surface-bound sulphide is accessible by the regenerant and oxidation to sulphate occurs. Sulphate in turn has no affinity to Pd metal [16,21,22] and, therefore, is released to the aqueous phase, freeing the active sites of the catalyst. Permanganate as a powerful regenerant for sulphide-deactivated Pd catalysts was recently reported by our group in Ref. [16]. This report did not, however, consider the pH value as a key parameter for the efficiency of the regeneration procedure. In the present study, Pd/Al_2O_3 was subjected to sulphide poisoning (S:Pd = 2 moles per mole) and subsequently to oxidative regeneration under various pH conditions. The poisoning was conducted under neutral, acidic, and alkaline conditions which resulted in the complete loss of catalyst activity. Permanganate was added to the catalyst suspensions at the corresponding pH values. The addition of sulphides and permanganate did not significantly change the pH values in the catalyst suspensions. It is important to note that after a given regeneration period, the unconsumed permanganate was quenched with hydrazine (instantaneous decolourisation of the suspension) before HDC tests were conducted. This is due to the inhibitory effect of permanganate on the HDC when present at higher than a threshold concentration of about 0.08 mM, as described in detail in Ref. [16]. The addition of hydrazine for quenching the unconsumed permanganate caused the pH value of the suspension to increase to pH ≈ 8 (for pH$_{regeneration}$ = 3) and pH 10 (for pH$_{regeneration}$ = 7), while under alkaline conditions the pH remained alkaline (pH ≈ 13). Therefore, these pH values were then taken as the starting pH of the bulk solution when the performance of the regenerated catalysts was probed.

The evaluation of the recovered catalyst performance shows a strong correlation between the applied pH values and the regeneration efficacy of permanganate. After 24 h of permanganate (0.18 mM) treatment at neutral conditions, the recovered catalyst activity for the complete dechlorination of MCB was around $71 \, L \, g^{-1} \, min^{-1}$, corresponding to about 60% of the original activity. Shorter regeneration times (e.g. 4 h) only delivered an unstable catalyst state. The HDC of MCB proceeded incompletely, i.e. the catalyst lost its activity during the course of the HDC reaction. This behaviour was typical of incompletely regenerated catalyst samples. It suggests a re-poisoning of the catalyst under the reducing reaction conditions. In Ref. [23] a long-term sulphur reservoir in the catalyst was discussed. The authors speculate on the diffusion of sulphur into Pd-clusters where the sulphur would be protected against short-term oxidation.

A different scenario was observed for the catalyst regenerated under acidic and alkaline conditions. 0.5 h of permanganate treatment at pH 13 resulted in the recovery of an initial catalyst activity of about $A_{Pd,1} = 40 \, L \, g^{-1} \, min^{-1}$ (Fig. 3). After 50 min the HDC rate slowed and the catalyst activity was reduced to $A_{Pd,2} = 20 \, L \, g^{-1} \, min^{-1}$. When the regeneration time with permanganate was increased to 5 h, the obtained catalyst activity was increased to $A_{Pd} = 58 \, L \, g^{-1} \, min^{-1}$ and the HDC reaction proceeded to completion without any further activity loss (Fig. 3). This magnitude of catalyst activity was also obtained for Pd/Al_2O_3 regenerated under neutral conditions, but this required a full day of regeneration as was mentioned above.

The most efficient regeneration of sulphide-fouled Pd/Al_2O_3 was obtained under acidic conditions (pH 3). This is demonstrated in Fig. 4, where short regeneration times of 10 min and 30 min
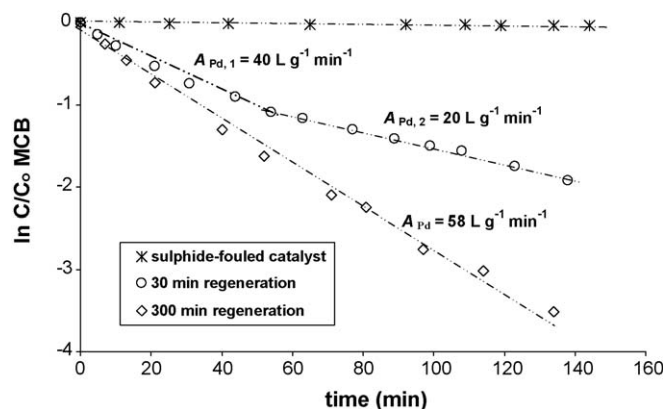
Fig. 3. Recovered catalyst activity (A_{Pd}) after oxidative regeneration of sulphide-fouled Pd/Al_2O_3 under alkaline conditions (pH 13). Regeneration was conducted using 0.18 mM $KMnO_4$ for 30 and 300 min (c_{cat} = 150 mg L^{-1}, $c_{0,MCB}$ = 20 mg L^{-1}).

completely recovered the catalyst activity (A_{Pd} = 132 and 466 L g^{-1} min^{-1}, respectively). It is remarkable that after 30 min of permanganate treatment and hydrazine quenching the catalyst exposed even higher activities than the baseline activity of the fresh catalyst (A_{Pd} = 120 L g^{-1} min^{-1}). This phenomenon was reproduced several times (A_{Pd} = 450 ± 100 L g^{-1} min^{-1}). It should be emphasized again, that dechlorination was conducted in the same reaction mixtures where the catalyst samples were first poisoned and then regenerated. This means that the observed exceptionally high reaction rates can be due either to the catalyst state or to the composition of the reaction medium. In order to distinguish between these two reasons another set of dechlorination experiments was conducted. This time, after the regeneration process, the catalyst was separated from the suspension by centrifugation and washed with deionized water. This catalyst sample was then added to a fresh reaction solution (DW with pH 7–8) containing H_2 in the headspace and MCB in the water phase. The catalyst delivered activities (A_{Pd} = 120 ± 10 L g^{-1} min^{-1}) in the range of the baseline activity of the fresh catalyst under neutral condition (cf. Table 1). Thus, the very high dechlorination rates with the regenerated catalyst under the employed conditions appeared only when the reaction was conducted in the regeneration matrix. The key components or parameters of this matrix responsible for the accelerating effect are not obvious. Hydrazine is known to be active as a reductant for the Pd-catalyzed HDC reaction. However, it was found to be effective only under alkaline conditions [29].

In order to further confirm the hypothesis that low pH values are a key requirement for efficient catalyst regeneration, an
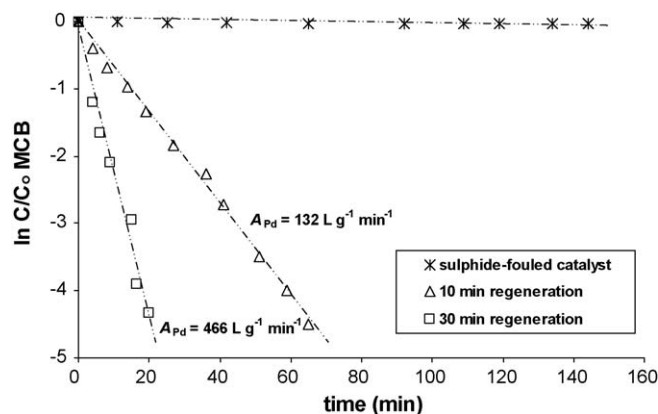
Fig. 4. Recovered catalyst activities (A_{Pd}) after oxidative regeneration of sulphide-fouled Pd/Al_2O_3 under acidic condition (pH 3). Regeneration was conducted using 0.18 mM $KMnO_4$ for 10 and 30 min (c_{cat} = 150 mg L^{-1}, $c_{0,MCB}$ = 20 mg L^{-1}).

additional experiment was conducted. This time the catalyst was poisoned with sulphide (14.2 μM) under neutral and regenerated under acidic conditions (pH 3; 0.18 mM KMnO$_4$). The results from this experiment showed again the recovery of a very high catalyst activity of about 400 L g^{-1} min^{-1} after only 30 min of regeneration time, similar to the data shown in Fig. 4. This confirms the strong pH-dependence of permanganate efficacy as regenerant for sulphide-fouled Pd/Al$_2$O$_3$ catalysts.

The fast and effective regeneration of sulphide-fouled Pd/Al$_2$O$_3$ under acidic conditions, as shown in Fig. 4, needs further elucidation. It should be taken into consideration that the active component Pd, the carrier Al$_2$O$_3$, the sulphur and manganese speciation are all susceptible to pH changes. Permanganate itself is reactive in a wide pH range. Under acidic conditions, the oxidation half-reaction is $MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$ with a standard oxidation potential of E° = 1.51 V. The reduction proceeds to the formation of Mn^{2+}, which is soluble in water. On the other hand, water-insoluble manganese dioxide (MnO$_2$) is the end product of the reduction of permanganate under neutral and basic conditions $(MnO_4^- + 2\ H_2O + 3\ e^- \rightarrow MnO_2 + 4\ OH^-$ with E° = 0.60 V). There are two plausible reasons for the observed pH effects: (i) the higher redox potential ('oxidation power') of permanganate under acidic conditions and (ii) the positive surface charge of alumina (pH$_{pzc}$ = 8.2) which may facilitate the access of the permanganate anion to the Pd sites. This is the kinetic aspect of the reaction, which may be even more significant than the thermodynamic aspect considered above. Apparently, both permanganate reduction products (i.e. dissolved Mn^{2+} at acidic pH and MnO$_2$ at neutral to alkaline pH) do not significantly deactivate the Pd catalyst.

Additional experiments were conducted in order to assess an optimal permanganate concentration at pH 3. According to the reaction stoichiometry $5\ H_2S + 8\ MnO_4^- + 2\ H_2O \rightarrow 5\ SO_4^{2-} + 8\ Mn^{2+} + 14\ OH^-$, the reagent concentrations usually applied (14.2 μM S^{2-} and 0.18 mM MnO$_4^-$) are equivalent to an 8-fold surplus of the oxidant, provided there are no other permanganate consumers in the catalyst suspension. When the permanganate concentration was reduced to 0.09 mM, an activity recovery of only 14% after 10 min regeneration was achieved but the full activity was regained after 60 min regeneration time. On the other hand, an increase of the oxidant concentration (e.g. to 0.36 mM) did not give rise to any significant improvement of the regeneration efficiency. That is, it neither shortens the regeneration time requirement nor increases the recovered catalyst activity. This implies that the permanganate-based regeneration procedure can be realized at a low concentration level (about 0.1 mM), depending mainly on the stoichiometric demand. For comparison, in the oxidative regeneration of sulphide-fouled catalysts using hypochlorite, much higher regenerant concentrations (in the range of 20–50 mM NaOCl) are usually employed [21–23]. In one study [21], the 'highly poisoned catalyst' (S to Pd molar ratio of 0.66, surface S content of Pd as determined by X-ray photoelectron spectroscopy), 56 mM NaOCl was used in order to restore the catalyst activity to about 29% of its original value. In this case, full recovery of catalyst reactivity was not easily achievable. It is worth mentioning that in the study of Munakata and Reinhard [23] on various catalyst regenerants, the applied Pd/Al$_2$O$_3$ catalyst with 1 wt% Pd had an apparent baseline activity ($A_{Pd} \approx 0.1$ L g^{-1} min^{-1}) which is three orders of magnitude lower than that of our catalyst. Therefore, it might be easier to achieve a partial regeneration there than for a highly active catalyst such as used in the present study. Furthermore, hypochlorite is a chlorinating agent and additional care must be taken during its employment as catalyst regenerant.

4. Conclusions

The presented paper describes the stability and sulphide-induced deactivation behaviour of a Pd/Al$_2$O$_3$ (0.5 wt% Pd) hydrodechlorination catalyst and its response to oxidative regeneration using potassium permanganate. Primarily, in sulphide-free clean water the catalyst did not show any inherent deactivation during repeated batch reaction cycles in the pH range 3–13. The addition of sulphides to the catalyst suspension led to the expected poisoning of the catalyst. The impact of the pH value on the deactivating effect of sulphides was relatively small but nevertheless showed that Pd/Al$_2$O$_3$ was more resistant to poisoning under acidic conditions. The exposure of the catalyst to higher sulphide doses (e.g. 14.2 μM, S:Pd$_{surface}$ = 12 moles per mole) resulted in a complete catalyst deactivation regardless of the applied pH conditions. The oxidative regeneration of the totally deactivated catalyst with permanganate showed consistently strong pH-dependence. Regeneration under neutral and basic conditions showed a complete but slow recovery of catalyst activity. When oxidative regeneration was conducted under acidic condition (pH 3) the fouled catalyst could be re-activated within a short time of 10–30 min with the complete recovery of its performance. Thus, we point out in our study the superiority of permanganate as regenerant for sulphide-fouled Pd/Al$_2$O$_3$.

References

[1] G.V. Lowry, M. Reinhard, Environ. Sci. Technol. 33 (1999) 1905.
[2] C. Schueth, S. Disser, F. Schueth, M. Reinhard, Appl. Catal. B 28 (2000) 147.
[3] C. Schueth, M. Reinhard, Appl. Catal. B 18 (1998) 215.
[4] K. Mackenzie, H. Frenzel, F.-D. Kopinke, Appl. Catal. B 63 (2006) 161.
[5] U. Prusse, K.D. Vorlop, J. Mol. Catal. A: Chem. 173 (2001) 149.
[6] M.G. Davie, M. Reinhard, J.R. Shapley, Environ. Sci. Technol. 40 (2006) 7329.
[7] K.D. Hurley, J.R. Shapley, Environ. Sci. Technol. 41 (2007) 2044.
[8] W.W. McNab Jr., R. Ruiz, M. Reinhard, Environ. Sci. Technol. 34 (2000) 149.
[9] N.E. Korte, J.L. Zutman, R.M. Schlosser, L. Liang, B. Gu, Q. Fernando, Waste Manage. 20 (2000) 687.
[10] C. Schueth, N.A. Kummer, C. Weidenthaler, H. Schad, Appl. Catal. B 52 (2004) 197.
[11] F.-D. Kopinke, R. Koehler, K. Mackenzie, H. Borsdorf, C. Schueth, Grundwasser 3 (2002) 140.
[12] D. Fritsch, K. Kuhr, K. Mackenzie, F.-D. Kopinke, Catal. Today 82 (2003) 105.
[13] D.R. Alfonso, A.V. Cugini, D.S. Sholl, Surf. Sci. 546 (2003) 12.
[14] D.R. Alfonso, A.V. Cugini, D.C. Sorescu, Catal. Today 99 (2005) 315.
[15] P.A. Gravil, H. Toulhoat, Surf. Sci. 430 (1999) 176.
[16] D. Angeles-Wedler, K. Mackenzie, F.-D. Kopinke, Environ. Sci. Technol. 42 (2008) 5734.
[17] J.M. Jones, V.A. Dupont, R. Brydson, D.J. Fullerton, N.N. Nasri, A.B. Ross, A.V.K. Westwood, Catal. Today 81 (2003) 589.
[18] T.-C. Yu, H. Shaw, Appl. Catal. B 18 (1998) 105.
[19] J.C. Rodriguez, J. Santamaria, A. Monzon, Appl. Catal. 165 (1998) 147.
[20] E. Lopez, F.V. Diez, S. Ordonez, Appl. Catal. B 82 (2008) 264.
[21] B.P. Chaplin, J.R. Shapley, C.J. Werth, Environ. Sci. Technol. 41 (2007) 5491.
[22] G.V. Lowry, M. Reinhard, Environ. Sci. Technol. 34 (2000) 3217.
[23] N. Munakata, M. Reinhard, Appl. Catal. B 75 (2007) 1.
[24] F.-D. Kopinke, K. Mackenzie, R. Koehler, Appl. Catal. B 44 (2003) 15.
[25] G. Yuan, M.A. Keane, J. Catal. 225 (2004) 510.
[26] M.A. Aramendia, R. Burch, I.M. Garcia, A. Marinas, J.M. Marinas, B.W.L. Southward, F.J. Urbano, Appl. Catal. B 31 (2001) 163.
[27] K. Bourikas, J. Vakros, C. Kordulis, A. Lycourghiotis, J. Phys. Chem. B 107 (2003) 9441.
[28] E. Marceau, X. Carrier, M. Che, O. Clause, C. Marcilly, in: G. Ertl, H. Knötzinger, F. Schüth, J. Weitkamp (Eds.), Handbook of Heterogenous Catalysis, second ed., VCH-Wiley, Weinheim, 2008, p. 470.
[29] F.-D. Kopinke, K. Mackenzie, R. Köhler, A. Georgi, Appl. Catal. A 271 (2004) 119.